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Relationship among thermal expansivity, isothermal bulk modulus and volume expansion ratio for ionic solids at high temperatures

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Abstract : In the present study, a new elementary relationship among α, K_T and (V_T/V_0) for ionic solids is reported. The solids considered are NaCl, KCl, MgO and CaO. The analysis is done at high temperatures with the help of the experimental data available. It is observed that $\alpha + nK_T(V_T/V_0)$ not $\alpha K_T(V_T/V_0)$, remains invariant in high temperature domain for solids under study. The present study also discloses that the Anderson-Gruneisen parameter increases with temperature in very high temperature domain. The results are valuable to understand the thermodynamic and thermoelastic properties of solids at high temperature.

Keywords : Thermal expansivity, isothermal bulk modulus, volume expansion ratio, ionic solids.

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1. Introduction

The theory of thermal expansivity plays a central role in describing the high temperature behaviour of solids. Several attempts have been made [1–8] to study the thermodynamic properties such as thermal expansivity, bulk modulus and volume ratio of solids under the effect of temperatures. Thermal expansivity and bulk modulus are very important thermodynamic quantities for understanding the high temperature behaviour and equation of state for solids [7]. The study of thermodynamic and thermoelastic behaviour of ionic solids at high temperatures requires the knowledge of thermal expansivity, isothermal bulk modulus and volume expansion ratio along with the Anderson-Gruneisen parameter. The experimental and generalized data on temperature dependence of thermodynamic quantities for ionic solids *viz.* NaCl, KCl, MgO and CaO have been reported by Anderson [9] and Singh and Chauhan [7], which are considered to be most accurate for the present study. The experimental data [9] show that the Debye temperature (θ_D) for NaCl and KCl are close to room temperature *i.e.* 304 K and 230 K, respectively whereas those for MgO and CaO are 945 K and 671 K, respectively.

The present study examines the thermodynamic and thermoelastic data of ionic solids *viz.* NaCl, KCl, MgO and CaO to detect a simple relationship among thermal expansivity (α), isothermal bulk modulus (K_T) and volume expansion ratio (V_T/V_0) at temperatures higher than the Debye temperature . The method of analysis is shown in Section 2 and results are discussed in Section 3.

2. Method of analysis

The experimental data reported by Anderson [9] show that the variance of thermal expansivity is nonlinear below the Debye temperature while it becomes linear in high temperature domain $(T \geq \theta_D)$. On the other hand, the isothermal bulk modulus is found to decrease with the increase in temperature. One of the most widely used thermodynamic approximations [4,10,11] for analyzing the high temperature/high pressure conduct of solids is as follows

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$$\alpha K_T = \text{Constant.} \quad (1)$$

Wang and Reeber [12] fitted a new set of experimental data on $\alpha K_T V_T$, constituting the partial temperature derivative of the work done by thermal pressure and applying modified Einstein Model. It is shown that $\alpha K_T V_T$, not αK_T, approaches a constant value at high temperature. Thus, we can write

$$\alpha K_T V_T = \text{Constant.} \quad (2)$$

Here, an effort has been made to plot αK_T against (V_T/V_0), $\alpha(V_T/V_0)$ against K_T, α against $K_T(V_T/V_0)$, $\ln \alpha K_T$ against $\ln(V_T/V_0)$, $\ln \alpha(V_T/V_0)$ against $\ln K_T$, $\ln \alpha$ against $\ln K_T(V_T/V_0)$, adopting the high temperature experimental data reported by Anderson [9] and extrapolated data reported by Singh and Chauhan [7], to look into the relationship among α, K_T and (V_T/V_0) for ionic solids under consideration. An orderly linear curve is obtained only for α *versus* $K_T(V_T/V_0)$ (Figures 1–4), resulting the following relationship

$$\alpha + nK_T(V_T/V_0) = \text{Constant}, \quad (3)$$

where n is a constant and have the dimension of (α/K_T). The value of n measured by the slope of the curves are shown in Tables 1–4 for corresponding solids. It should be emphasized that (V_T/V_0) is the ratio of volume at temperature T to volume at 300 K.

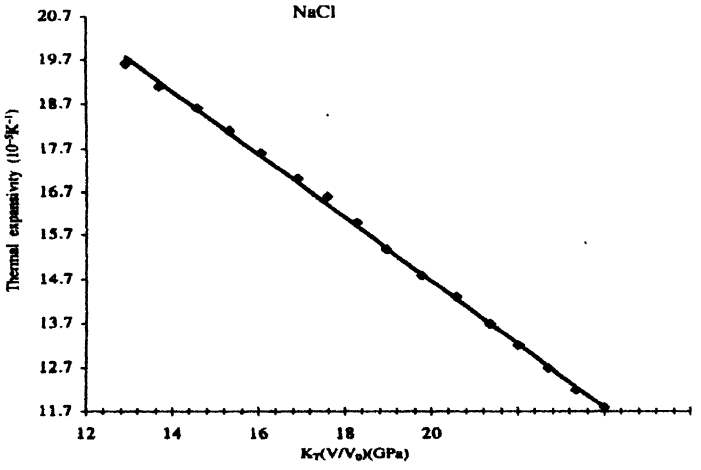

Figure 1. Plot of thermal expansivity (α) *versus* $K_T(V_T/V_0)$ at high temperatures.

Now differentiating eq. (3) with respect to temperature T on isobaric condition, we get

$$\frac{d\alpha}{dT} + n\frac{d}{dT}\left[K_T\left(\frac{V_T}{V_0}\right)\right] = 0 \quad (4)$$

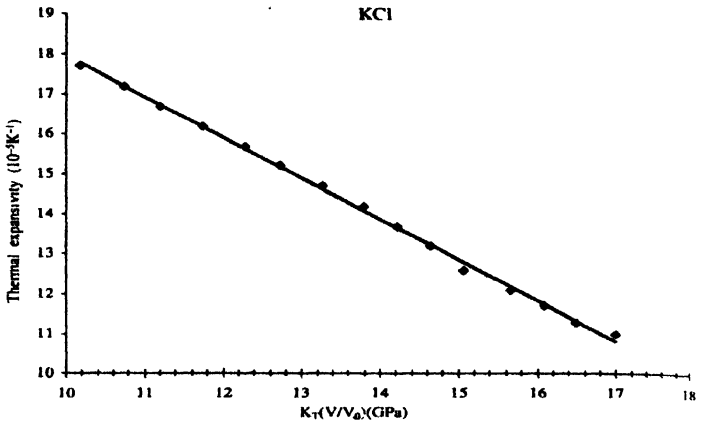

Figure 2. Plot of thermal expansivity (α) *versus* $K_T(V_T/V_0)$ at high temperatures.

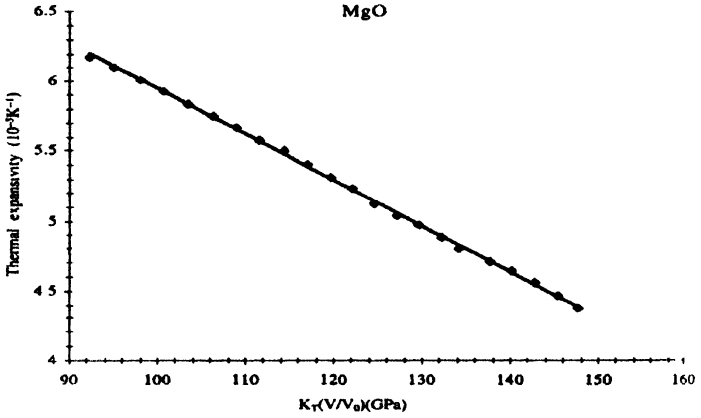

Figure 3. Plot of thermal expansivity (α) *versus* $K_T(V_T/V_0)$ at high temperatures.

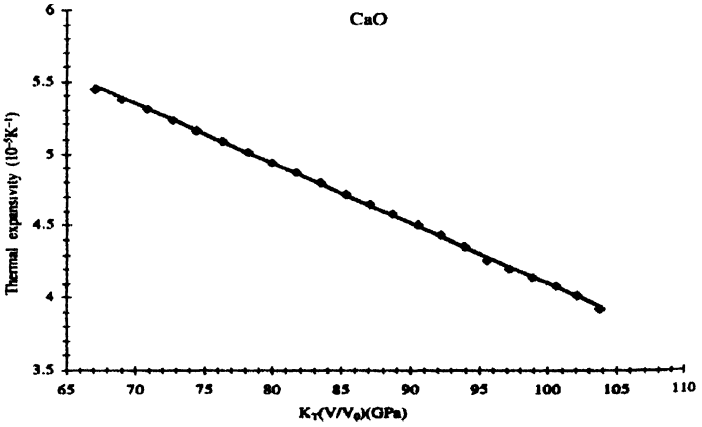

Figure 4. Plot of thermal expansivity (α) *versus* $K_T(V_T/V_0)$ at high temperatures.

It is found [7,9] that thermal expansivity varies linearly with temperature in high temperature domain. Thus, it may be written as

Table 1. Computed values of $\alpha K_T(V_T/V_0)$, $\alpha + nK_T(V_T/V_0)$ and δ_T. The input data are adopted from Anderson [9] and Singh and Cahauhan [7] for NaCl : $n = 0.7194 \times 10^{-5}$ K^{-1}(Gpa)$^{-1}$, $\delta_T^* = 5.56$.

T(K)	$\alpha(10^{-5}$ K$^{-1})$	(V_T/V_0)	K_T(Gpa)	$\alpha K_T(V_T/V_0)$	$\alpha+nK_T(V_T/V_0)$	δ_T
300	11.8	1.0000	24.0	283.20	29.07	5.56
350	12.2	1.0061	23.2	284.77	28.99	5.53
400	12.7	1.0127	22.4	288.09	29.02	5.48
450	13.2	1.0194	21.6	290.65	29.04	5.44
500	13.7	1.0261	20.8	292.40	29.05	5.42
550	14.3	1.0335	19.9	294.10	29.10	5.39
600	14.8	1.0410	19.0	292.73	29.03	5.41
650	15.4	1.0486	18.1	292.29	29.05	5.42
700	16.0	1.0568	17.3	292.52	29.15	5.41
750	16.6	1.0657	16.5	291.90	29.25	5.42
800	17.0	1.0747	15.7	286.84	29.14	5.50
850	17.6	1.0841	14.8	282.39	29.14	5.57
900	18.1	1.0938	14.0	277.17	29.12	5.66
950	18.6	1.1038	13.2	271.00	29.08	5.77
1000	19.1	1.1143	12.3	261.78	28.96	5.93
1050	19.6	1.1251	11.5	253.60	28.91	6.09

Table 2. Computed values of $\alpha K_T(V_T/V_0)$, $\alpha + nK_T(V_T/V_0)$ and δ_T. The input data are adopted from Anderson [9] and Singh and Cahauhan [7] for KCl : $n = 1.0174 \times 10^{-5}$ K^{-1}(Gpa)$^{-1}$, $\delta_T^* = 5.84$.

T(K)	$\alpha(10^{-5}$ K$^{-1})$	(V_T/V_0)	K_T(Gpa)	$\alpha K_T(V_T/V_0)$	$\alpha+nK_T(V_T/V_0)$	δ_T
300	11.0	1.0000	17.0	187.00	28.30	5.84
350	11.3	1.0056	16.4	186.36	28.08	5.86
400	11.7	1.0117	15.9	188.21	28.07	5.81
450	12.1	1.0175	15.4	189.60	28.04	5.77
500	12.6	1.0243	14.7	189.72	27.92	5.77
550	13.2	1.0307	14.2	193.19	28.09	5.68
600	13.7	1.0377	13.7	194.77	28.16	5.65
650	14.2	1.0448	13.2	195.84	28.23	5.62
700	14.7	1.0526	12.6	194.96	28.19	5.64
750	15.2	1.0605	12.0	193.44	28.15	5.68
800	15.7	1.0685	11.5	192.92	28.20	5.69
850	16.2	1.0772	10.9	190.21	28.15	5.76
900	16.7	1.0867	10.3	186.92	28.09	5.84
950	17.2	1.0960	9.80	184.74	28.13	5.90
1000	17.7	1.1056	9.20	180.04	28.05	6.03

$$\frac{d\alpha}{dT} = C \text{ (Constant)}. \tag{5}$$

Using the above condition, eq. (4) generates

$$\frac{d}{dT}\left[K_T\left(\frac{V_T}{V_0}\right)\right] = -D, \tag{6}$$

Table 3. Computed values of $\alpha K_T(V_T/V_0)$, $\alpha + nK_T(V_T/V_0)$ and δ_T. The input data are adopted from Anderson [9] and Singh and Cahauhan [7] for MgO : $n = 0.0327 \times 10^{-5}$ K^{-1}(Gpa)$^{-1}$, $\delta_T^* = 4.78$.

T(K)	$\alpha(10^{-5}$ K$^{-1})$	(V_T/V_0)	K_T(Gpa)	$\alpha K_T(V_T/V_0)$	$\alpha+nK_T(V_T/V_0)$	δ_T
900	4.38	1.024	144.3	647.20	9.21	4.78
1000	4.47	1.0284	141.4	650.01	9.23	4.76
1100	4.56	1.0331	138.3	651.52	9.23	4.75
1200	4.65	1.0379	135.1	652.02	9.24	4.75
1300	4.71	1.0428	132.1	648.82	9.21	4.77
1400	4.80	1.0476	128.1	644.15	9.19	4.80
1500	4.89	1.0529	125.7	647.19	9.22	4.78
1600	4.98	1.0582	122.5	645.55	9.22	4.79
1700	5.04	1.0635	119.6	641.06	9.20	4.82
1800	5.13	1.0689	116.6	639.37	9.21	4.83
1900	5.24	1.0745	113.7	640.17	9.23	4.82
2000	5.32	1.0801	110.7	636.10	9.23	4.85
2100	5.41	1.0860	107.7	632.77	9.23	4.87
2200	5.50	1.0919	104.7	628.77	9.24	4.89
2300	5.58	1.0980	101.7	623.10	9.23	4.93
2400	5.67	1.1042	98.7	617.94	9.23	4.96
2500	5.75	1.1105	95.7	611.08	9.23	5.00
2600	5.84	1.1169	92.7	604.65	9.23	5.05
2700	5.93	1.1235	89.7	597.61	9.23	5.09
2800	6.01	1.1302	86.7	588.91	9.21	5.15
2900	6.10	1.1371	83.7	580.57	9.21	5.21
3000	6.18	1.1441	80.7	570.59	9.20	5.29

Table 4. Computed values of $\alpha K_T(V_T/V_0)$, $\alpha + nK_T(V_T/V_0)$ and δ_T. The input data are adopted from Anderson [9] and Singh and Cahauhan [7] for CaO : $n = 0.0417 \times 10^{-5}$ K^{-1}(Gpa)$^{-1}$, $\delta_T^* = 5.07$.

T(K)	$\alpha(10^{-5}$ K$^{-1})$	(V_T/V_0)	K_T(Gpa)	$\alpha K_T(V_T/V_0)$	$\alpha+nK_T(V_T/V_0)$	δ_T
700	3.92	1.0145	102.3	406.83	8.25	5.07
800	4.01	1.0186	100.3	409.68	8.27	5.04
900	4.08	1.0226	98.4	410.55	8.28	5.03
1000	4.14	1.0267	96.3	409.33	8.26	5.05
1100	4.20	1.0311	94.3	408.38	8.25	5.05
1200	4.26	1.0356	92.3	407.20	8.25	5.07
1300	4.36	1.0401	90.3	409.50	8.28	5.04
1400	4.43	1.0446	88.3	408.62	8.28	5.05
1500	4.50	1.0493	86.3	407.50	8.28	5.06
1600	4.58	1.0541	84.2	406.50	8.28	5.07
1700	4.65	1.0590	82.2	404.78	8.28	5.09
1800	4.72	1.0639	80.2	402.73	8.28	5.11
1900	4.80	1.0690	78.1	400.75	8.28	5.13
2000	4.87	1.0742	76.1	398.11	8.28	5.16
2100	4.94	1.0795	74.1	395.16	8.28	5.19
2200	5.01	1.0849	72.1	391.89	8.27	5.23
2300	5.09	1.0904	70.0	388.51	8.27	5.26
2400	5.16	1.0960	68.0	384.56	8.27	5.31
2500	5.23	1.1017	66.0	380.28	8.26	5.35
2600	5.31	1.1075	64.0	376.37	8.27	5.40
2700	5.38	1.1134	62.0	371.39	8.26	5.46
2800	5.45	1.1195	59.9	365.47	8.25	5.53

where

$$D = -(C/n). \tag{7}$$

Solving eq. (6), we obtain

$$\frac{K_T}{V_0}\left(\frac{dV}{dT}\right) + \frac{V_T}{V_0}\left(\frac{dK_T}{dT}\right) = -D \tag{8}$$

Employing the basic numerical definition of thermal expansivity and the Anderson-Gruneisen parameter, as follows

$$\alpha = -\frac{1}{V_T}\frac{dV_T}{dT} \tag{9}$$

and

$$\delta_T = -\frac{1}{\alpha K_T}\left(\frac{dK_T}{dT}\right) \tag{10}$$

in eq. (8), we get the following relationship :

$$(\delta_T - 1) = \frac{D}{\alpha K_T (V_T/V_0)}. \tag{11}$$

Applying the initial conditions *i.e.* at $T = T^* \geq \theta_D$, $\alpha = \alpha^*$, $K_T = K_T^*$, $V_T = V^*$ and $\delta_T = \delta_T^*$, we get following relationship for the Anderson-Gruneisen parameter :

$$\delta_T = 1 + (\delta_T^* - 1)\left[\frac{\alpha^* K_T^* V^*}{\alpha K_T V_T}\right]. \tag{12}$$

The above relation represents the variation of δ_T in high temperature region in terms of active parametric quantities.

3. Results and discussion

The authoritative finding of the present work is that $\alpha + nK_T(V_T/V_0)$ is found to remain constant in high temperature area. On the other hand, the product $\alpha K_T(V_T/V_0)$ is found to vary with temperatures. The close investigation of data reveals that at temperature near $2\theta_D$, the product $\alpha K_T(V_T/V_0)$ decreases continuously with temperature. The data, which confirms the present analytical approach, are shown in Tables 1–4 for ionic solids under consideration. The eq. (12) brings about a method to predict the values of the Anderson-Gruneisen parameter. In the present study, the values of δ_T applying eq. (12) are evaluated at high temperatures and value of δ_T^* are drawn out from the experimental data [9]. The calculated values of δ_T are listed in last column of Tables 1–4 for corresponding ionic solid. It was adopted [9] that δ_T remains constant with temperature but the present study shows that at higher temperature, δ_T increases with temperature. The present study might be used to predict the high temperature properties of solids.

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